PATENT SPECIFICATION

(11) 1322959

DRAWINGS ATTACHED

(21) Application No. 50791/70 (22) Filed 26 Oct. 1970

(31) Convention Application No. 85230 (32) Filed 27 Oct. 1969 in

(33) Japan (JA)

(44) Complete Specification published 11 July 1973

(51) International Classification H01M 27/16

(52) Index at acceptance H1B F11 F300

(19)

1322959

(54) SOLID ELECTROLYTE

(71) We, HITACHI LTD., of 1—5—1, Marunouchi, Chiyoda-ku, Tokyo, Japan, a Japanese Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a solid electrolyte and more particularly to a solid electrolyte suitable for use in fuel cells.

A conventional known solid electrolyte consists of a solid solution mainly of zirconium oxide in which is included 3 to 20% by mol of calcium oxide or a rare earth oxide, such as yttrium oxide or ytterbium oxide, to stabilize the electrolyte in a cubic form as well as to impart electrical conductivity to the oxygen ions in the solid solution. A solid electrolyte is a chemically stable substance having a small electrical resistance, and one which has an ion transference number close to 1 is preferred.

It is said that a solid electrolyte suitable for use in fuel cells desirably has an electrical resistance smaller than several tens of ohms or a specific resistance smaller than about 40Ω cm. Electrical resistance of an electrolyte generally tends to decrease as the temperature increases so that in order to render operable a fuel cell employing the known solid electrolyte described above, it has been necessary to hold the fuel cell at least to a temperature as high as 900 to 1,000°C. Therefore, a fuel cell including such a solid electrolyte has disadvantages as set forth below:

(1) Since the cell is operated at such a high temperature the materials of the cell are required to have excellent heat resistance and since such materials, for example, platinum, are generally expensive, the cost of the cell becomes high.

(2) The proportion of heat insulating parts used for maintaining the high temperature with respect to other component parts of the cell becomes particularly large.

Consequently, the volume and weight of the cell becomes large and the energy density per unit volume or unit weight of the cell is low.

(3) A large amount of heat must be supplied and, therefore, the running and maintenance cost becomes high because the parts which participate in the electro-chemical reaction in the cell must always be maintained at a high temperature.

(4) A longer time is required for commencing operations of the cell as the operation temperature of the cell becomes higher.

(5) Since this type of fuel cell is generally operated at a high temperature, metal oxide can readily diffuse in the solid electrolyte at a high velocity so that when a metal oxide is used as the electrode catalyst such diffusion of metal oxide accelerates the deterioration of solid electrolyte, with the accompanying result that the service life of the cell is shortened.

It would, therefore, be desirable to have a solid electrolyte which has an excellent oxygen ion conductive characteristic and a small specific resistance at a comparatively low temperature.

According to the present invention, there is provided a solid electrolyte consisting essentially of a solid solution having a lattice constant or range from 5.41 to 5.48 angstrom (taken to the second decimal place) measured at room temperature and represented by the general formula:

$$(CeO_2)_{1-x}[(Ln_{1-y}L'n_y)O_{1.5}]_x\ (MgO)_z$$

wherein Ln is at least one element selected from the group consisting of La, Nd, Sm, Eu and Dy; L'n is at least one elements selected from the group consisting of Y, Gd, Ho, Er, Tm, Yb and Lu; $0.05 \leqq x \leqq 0.3$; $0 \leqq y < 1$; and $0 \leqq z \leqq 0.05$. Such a solid solution has a fluorite structure.

Such a solid electrolyte of the present invention can be readily obtained by the ordinary firing method.

Namely, the solid electrolyte can be obtained by a process which comprises weighing

the respective raw materials individually so as to formulate a composition which satisfies the general formula given above, thoroughly mixing the raw materials, shaping the mixture into a desired shape by adding thereto a suitable binder, for example, polyvinyl alcohol, firing the shaped product for several hours at 1700 to 1850°C., and cooling it to room temperature.

The raw materials used for preparing the solid electrolyte are not necessarily restricted to oxides only but any compounds which can be readily converted into oxides on firing, such as, for example, oxalates and carbonates, may be used.

The present invention will now be described in greater detail with reference to the accompanying drawings which include preferred examples of the invention.

Fig. 1 shows specific resistance-lattice constant curves for different examples of the present invention and

Fig. 2 shows characteristic curves of the lattice constant of a solid electrolyte with respect to the amount of Ln and L'n added to the solid electrolyte.

Referring first to Fig. 1, the curves show the relationship between the lattice constant (measured at room temperature) and the specific resistance at different temperatures in solid electrolytes of the present invention.

Curve 1 shows the specific resistance measured at 700°C., curve 2 at 750°C., curve 3 at 800°C., and curve 4 at 900°C.

The specific resistance of a solid electrolyte having a given lattice constant was measured at different temperatures to give the curves. Each of the temperature curves shows a similar tendency with respect to the relationship between the lattice constant and the specific resistance.

As is clear from the various curves in Fig. 1, the inventors found that the specific resistance of a CeO_2 system solid electrolyte is a function of the lattice constant.

A solid electrolyte having a lattice constant in the range from 5.41 to 5.48 angstrom, the specific resistance of which is smaller than 40Ω cm and the oxygen ion transference number of which is 0.98 or greater at a temperature above 700°C., is well suited for use as a solid electrolyte for a fuel cell at that temperature.

A solid electrolyte having a desired lattice constant can be readily obtained by controlling the amount of Ln or of the combination of Ln and L'n.

If Ln is added to CeO_2, the lattice constant of the CeO_2 system solid electrolyte generally increases, while if L'n without Ln is added to CeO_2, the lattice constant of that decreases.

An addition of Gd to CeO_2 hardly affects the lattice constant but it does influence the transference number of the oxygen ion.

An addition of MgO to CeO_2 not only influences the lattice constant but also the transference number of the oxygen ion. Up to 5 mol per cent, preferably 0.1 to 3 mol per cent of MgO provides very effective results on firing for producing a dense solid electrolyte.

Referring now to Fig. 2, there is shown the relationship between the lattice constant and values of the additional amount, x, of Ln alone (y=0), L'n (y=1), or of the combination of Ln and L'n in relation to CeO_2; curve 1 shows the relationship when the solid electrolyte is represented by the composition formula $(CeO_2)_{1-x}\,(LaO_{1.5})_x$ i.e. y=0; curve 2 shows the relationship when the solid electrolyte is represented by the composition formula $(CeO_2)_{1-x}\,[(La_{0.5}\,Y_{0.5})O_{1.5}]_x$; curve 3 shows for comparison the relationship when the solid electrolyte is represented by the composition formula $(CeO_2)_{1-x}(GdO_{1.5})_x$ i.e. y=1 (outside the invention); and curve 4 shows for comparison the relationship when the solid electrolyte is represented by the composition formula $(CeO_2)_{1-x}\,(YO_{1.5})_x$, i.e. y=1 and the lattice constant falls below 5.41, (outside the invention).

These curves are shown as representative examples of Ln and L'n, respectively. As may be apparent from Fig. 2, an element Ln has characteristics which increase the lattice constant of the electrolyte. Therefore, a solid electrolyte having a desired lattice constant can be obtained by controlling the additional amount of Ln. However, an element L'n has characteristics which decrease the constant so that, it may be necessary to use a combination of Ln and L'n.

In the present invention the value of x is one of the important factors as well as the lattice constant for obtaining a good solid electrolyte.

The value of x exerts a considerable influence on ionic conductivity. It appeared that in all cases where x is smaller than 0.05 or larger than 0.3, the ionic conductivity dropped remarkably; therefore, x should be maintained in the range from 0.05 to 0.3 for accomplishing the purpose of the present invention.

The solid electrolyte of this invention can be highly advantageously used, not only in a fuel cell as described above but also in various apparatus, e.g. an oxygen refiner and an apparatus for measuring the partial pressure of oxygen gas, in which an electrochemical reaction is used.

Example

Solid electrolytes of various compositions were produced by the following process.

Namely, the respective oxides of the proportions shown in Table 1 below are mixed as the raw materials, and each mixture is thoroughly mixed and ground in a ball mill for several hours.

Thereafter, each mixture is subjected to a preliminary firing in air at 1200 to 1300°C. for 8 hours to form a solid body and the thus formed solid body is again ground and mixed thoroughly in a ball mill for several hours. After adding polyvinyl alcohol as a binder, the powder thus obtained is pressure-moulded into a disc shape and the shaped product subjected to a final firing in air at 1750°C. for 2 hours when MgO is present in the raw materials, but when it is not present ($z=0$), at 1850°C. for 2 hours.

As stated above, the addition of MgO to the raw materials has the effect of reducing the firing temperature by 50 to 100°C. as compared with a sample without MgO.

Upon examining the crystal structure by X-ray diffraction, it was revealed that each sample of solid electrolyte was a solid solution having the fluorite structure.

It was also confirmed that the solid electrolyte permits only oxygen ions to permeate therethrough and the transference number of the oxygen ions is at least 0.98 or greater and is substantially close to 1 at a temperature of more than 700°C. In other words, such a solid electrolyte has an excellent oxygen ion conductive characteristic while its electron conductivity is negligibly low.

Also, the lattice constants were determined by X-ray diffraction at room temperature.

These solid electrolytes have the lattice constant and the specific resistance characteristics at various temperatures shown in Table 1.

TABLE I

Sample No.	Chemical Composition	Lattice Constant a_0(Å)	Specific Resistance (Ω cm) 700°C	750°C	800°C	900°C	
1	$(CeO_2)_{0.70}(Yb_2O_3)_{0.15}(MgO)_{0.03}$ (y = 1)	5.347	60.0	28.0	19.0	12.0	out of invention
2	$(CeO_2)_{0.70}(Er_2O_3)_{0.07}(Tm_2O_3)_{0.03}(Lu_2O_3)_{0.05}(MgO)_{0.03}$ (y = 1)	5.385	58.0	28.0	19.0	11.5	"
3	$(CeO_2)_{0.70}(Dy_2O_3)_{0.15}(MgO)_{0.03}$ (y = 0)	5.406	40.0	21.0	15.0	9.0	within invention
4	$(CeO_2)_{0.70}(Dy_2O_3)_{0.075}(Gd_2O_3)_{0.075}(MgO)_{0.03}$ (y = 0.5)	5.417	34.0	17.0	11.5	6.6	"
5	$(CeO_2)_{0.70}(Eu_2O_3)_{0.15}$ (y = 0)	5.433	22.0	13.0	8.8	5.1	"
6	$(CeO_2)_{0.70}(Eu_2O_3)_{0.15}(MgO)_{0.03}$ (y = 0)	5.433	22.0	13.0	8.8	5.1	"
7	$(CeO_2)_{0.70}(Sm_2O_3)_{0.12}(Ho_2O_3)_{0.015}(Y_2O_3)_{0.015}(MgO)_{0.03}$ (y = 0.2)	5.434	22.0	12.7	8.8	5.1	"
8	$(CeO_2)_{0.70}(Sm_2O_3)_{0.15}(MgO)_{0.03}$ (y = 0)	5.442	20.0	12.8	9.2	5.3	"
9	$(CeO_2)_{0.70}(Nd_2O_3)_{0.10}(Sm_2O_3)_{0.025}(Er_2O_3)_{0.025}(MgO)_{0.03}$ (y = $^1/_6$)	5.450	20.0	15.0	10.0	6.0	"
10	$(CeO_2)_{0.70}(Nd_2O_3)_{0.15}(MgO)_{0.03}$ (y = 0)	5.460	25.0	16.5	11.5	6.6	"
11	$(CeO_2)_{0.80}(La_2O_3)_{0.10}(MgO)_{0.03}$ (y = 0)	5.472	32.0	18.0	13.5	8.5	"
12	$(CeO_2)_{0.70}(La_2O_3)_{0.12}(Yb_2O_3)_{0.02}(Tm_2O_3)_{0.01}$ (y = 0.2)	5.475	34.0	19.0	14.0	8.9	"
13	$(CeO_2)_{0.70}(Nd_2O_3)_{0.075}(La_2O_3)_{0.075}(MgO)_{0.03}$ (y = 0)	5.480	36.0	20.0	14.5	9.2	"
14	$(CeO_2)_{0.70}(La_2O_3)_{0.15}(MgO)_{0.03}$ (y = 0)	5.510	90.0	58.0	36.0	16.5	out of invention

In Table 1, sample numbers 3 to 13 are examples of the present invention and sample numbers 1, 2 and 14 are examples for reference respectively, it will be noted that Samples 1 and 2 have $y=1$ and a lattice constant below 5.41 while in Sample 14 the lattice constant is above 5.48.

It will be clear from the above examples that the specific resistances of the solid electrolyte can be represented as a function of the lattice constant.

Namely those solid electrolytes having lattice constants in the range from 5.41 to 5.48 angstrom have excellent characteristics, specific resistances being smaller than 40Ω cm. at 700°C.

The solid electrolytes within the present invention having the good specific resistance-temperature characteristics as described above, when used in a fuel cell, have the advantage that the fuel cell can be operated at a temperature as low as 600 to 800°C., which is 200 to 300°C. lower than the operational temperature of the conventional fuel cell. Therefore, it is possible not only to reduce the production cost of the fuel cell relative to the conventional one, but also to reduce the maintenance cost of the cell since the cell is operable at a relatively low temperature.

WHAT WE CLAIM IS:—

1. A solid electrolyte consisting essentially of a solid solution having a lattice constant between 5.41 and 5.48 angstrom (taken to the second decimal place) measured at room temperature, represented by the general formula:

$$(CeO_2)_{1-x}[(Ln_{1-y}L'n_y)O_{1.5}]_x\ (MgO)_z$$

wherein Ln is at least one element selected from La, Nd, Sm, Eu and Dy; L'n is at least one element selected from Y, Gd, Ho, Er, Tm, Yb and Lu; $0.05 \leqq x \leqq 0.3$; $0 \leqq y < 1$; and $0 \leqq z \leqq 0.05$.

2. A solid electrolyte according to claim 1 in which y is zero.

3. A solid electrolyte according to claim 1 in which x is 0.3.

4. A solid electrolyte according to claim 1 in which $y=0$ and $x=0.3$.

5. A solid electrolyte according to claim 1 consisting of a solid solution represented by the formula $(CeO_2)_{1-x}[(La_{0.5}Y_{0.5})O_{1.5}]_x$.

6. A solid electrolyte according to claim 1 consisting of a solid solution represented by the formula $(CeO_2)_{0.70}(SmO_{1.5})_{0.3}(MgO)_{0.03}$.

7. A solid electrolyte according to claim 1 consisting of a solid solution represented by the formula

$$(CeO_2)_{0.70}[(Sm_{0.8}HO_{0.1}Y_{0.1})O_{1.5}]_{0.30}\ (MgO)_{0.30}.$$

8. A solid electrolyte according to claim 1 consisting of a solid solution represented by the formula $(CeO_2)_{0.70}(EuO_{1.5})_{0.3}\ (MgO)_{0.30}$.

9. A solid electrolyte according to claim 1 consisting of a solid solution represented by the formula $(CeO_2)_{0.70}(EuO_{1.5})_{0.30}$.

10. A solid electrolyte according to claim 1 substantially as herein described and exemplified with reference to the accompanying drawings.

11. A fuel cell incorporating a solid electrolyte as defined in any one of the preceding claims.

MEWBURN ELLIS & CO.,
Chartered Patent Agents,
70—72 Chancery Lane,
London, W.C.2.
Agents for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1973.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

FIG. 1

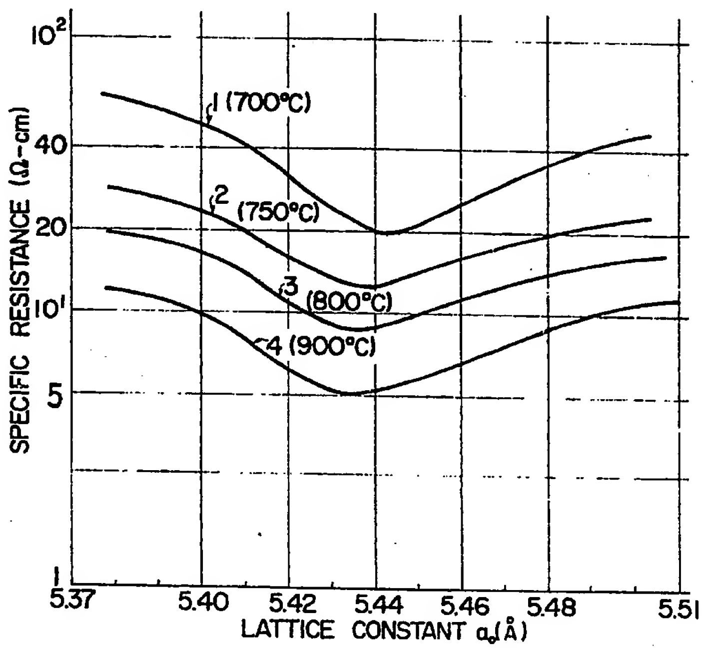
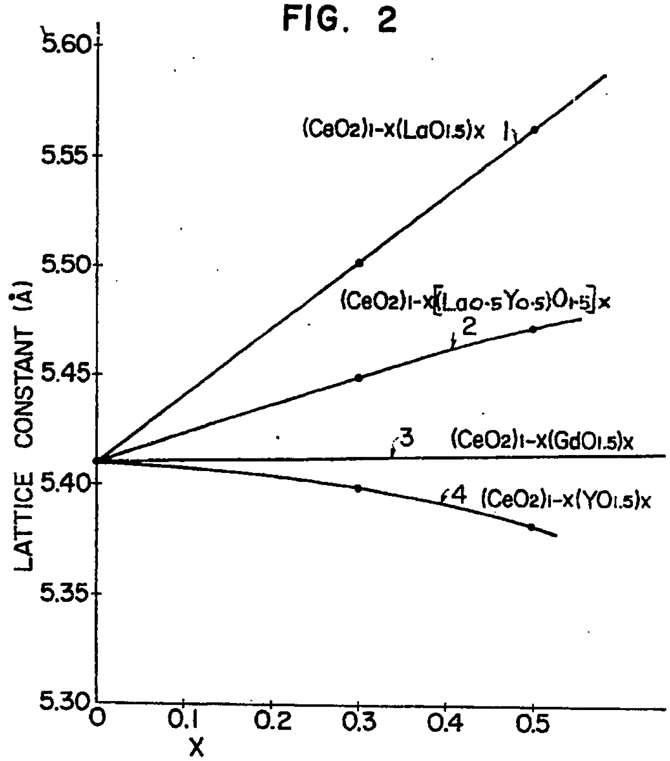

SPECIFIC RESISTANCE (Ω-cm)
LATTICE CONSTANT a₀(Å)
1 (700°C)
2 (750°C)
3 (800°C)
4 (900°C)
10²
40
20
10¹
5
1
5.37
5.40
5.42
5.44
5.46
5.48
5.51

FIG. 2


5.60
5.55
5.50
5.45
5.40
5.35
5.30
LATTICE CONSTANT (Å)
0
0.1
0.2
0.3
0.4
0.5
X
(CeO2)1-x(LaO1.5)x 1
(CeO2)1-x[(La0.5Y0.5)O1.5]x
2
3 (CeO2)1-x(GdO1.5)x
4 (CeO2)1-x(YO1.5)x